# ORDERING TRANSITIONS IN SYMMETRICAL MOLECULES

EDGAR F. WESTRUM, JR

*Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.*

## INTRODUCTION

Since Pauling's[1] original suggestion that certain types of solid–solid transitions might be explained by the onset of rotation in the crystalline state, many investigations have been carried out in an attempt to determine the nature of the mechanism of such transitions. Although originally the rotational freedom was attributed only to relatively simple molecules, Smyth[2, 3], through extensive investigations of the dielectric constants of compounds showing transitions, extended Pauling's view to include many larger and more complex molecules.

Perhaps the most extensive investigations have concerned the transitions in the ammonium halides. Apart from methane and some diatomic molecules, which are extremely difficult to study experimentally because of the low temperatures necessary for investigations, these compounds were considered to have the greatest probability of rotation in the solid state[1, 3]. Recent neutron diffraction investigations on the deuterated ammonium halides[4, 5], however, indicate that these transitions are explained as well by an order–disorder type of mechanism as by a rotational one[6]. Examination of the data for other compounds having solid–solid transitions shows that the results of experimental work in general neither prove nor disprove the existence of rotation in the solid state, but are equally consistent with the order–disorder mechanism for the transitions. Precise treatment of specific solid–solid transitions is greatly hindered by lack of accurate structural data, especially in the low-temperature region. These compounds are examples of relatively simple transitions because of the symmetry features of the ammonium ion.

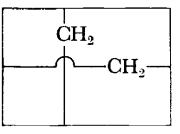
In solid–solid " pseudo-rotational " transitions in general, however, the structures, both molecular and crystallographic, are so complicated that no adequate correlation has been demonstrated between the isothermal entropy increments and structure changes at the transition temperatures. In transitions involving more complex molecules, the factors to be considered are apparently more convenient to study because of the larger number of possible comparison compounds which may be synthesized.

Two types of symmetrical molecules were considered to be of special interest at the outset of our researches on this interesting problem. Professor Isamu Nitta directed our attention to his extensive studies on pentaerythritol and to the pseudo-rotational problem in general. Dr Donald H. Payne (now of E. I. du Pont de Nemours) collaborated in this work and completed his doctoral thesis on compounds of the general type $C(CH_2X)_4$ (where X may represent halogen or hydrogen atoms, or hydroxyl groups).

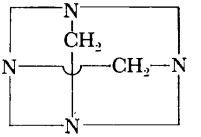
Solid–solid transitions have been studied in neopentane, $C(CH_3)_4$, by Aston[7] and in pentaerythritol, $C(CH_2OH)_4$, by Nitta[8–11]; the latter compound has a remarkably high entropy of transition. Comparison of the symmetry features of the high-temperature cubic modification of pentaerythritol with the symmetry features of neopentane, $C(CH_3)_4$, suggested that the symmetrical tetrahalide homologues of pentaerythritol would be interesting compounds for investigation. Although no transitions were reported in the literature for pentaerythrityl chloride, bromide, or iodide, synthesis of the pentaerythrityl fluoride, $C(CH_2F)_4$, was expected to produce a compound showing a low-temperature transition with a transition entropy increment intermediate between that of pentaerythritol and that of neopentane. Although the transition in pentaerythritol occurs at 180°C, the fluorine analogue should have a transition in the relatively low temperature region (below room temperature) because of the absence of the strong hydrogen bonds present in pentaerythritol.

The primary purpose of the problem investigated by Dr Payne, therefore, was the study of the low-temperature thermodynamic properties of the pentaerythrityl fluoride relative to the nature of the transitions occurring in the general compounds $C(CH_2X)_4$. By measuring the entropy for the predicted transition in this compound it was hoped to provide data for comparison with pentaerythritol and neopentane relative to the mechanism of the transitions in these compounds, in addition to the possible indication of a more general correlation applicable to this type of solid–solid transition.

Compounds of a second type are being studied by Mr Shu-Sing Chang. These are the unusual globular molecules such as the hydrocarbon adamantane (A), hexamethylenetetramine (B), and related organic molecules with nitrogen, sulphur, oxygen, and phosphorus substituted into the cage structure.




(A)




(B)

These compounds are characterized by extremely high melting points for organic solids (e.g., 270°C for adamantane) and probably by low entropy increments on fusion. Moreover, from the point of view of the chemist, the loss of the high symmetry factor in compound or complex formation provides an additional driving force in chemical reactions. An energetic transition was discovered at 208·6°K in adamantane soon after a synthetic method for the preparation of this substance became known to us.

## THE CALORIMETRIC APPARATUS

The Mark I cryostat for use over the range 4°–350°K was an improved version of one constructed by Westrum, Hatcher, and Osborne[12]. Liquid helium was used as the lowest temperature refrigerant, and a thermal conduction resistance (called the " economizer ") was provided to take advantage of the relatively large cooling potential of the enthalpy of gaseous helium

(compared with the heat of vaporization). The adiabatic method of operation was employed.

The gold-plated copper calorimeter (Laboratory Designation W–6) used for the pentaerythritol derivatives was 3·8 cm in diameter and 7·7 cm long with a shell thickness of 0·4 mm. Eight radial vanes of 0·1 mm copper foil aided in establishing thermal equilibrium. A re-entrant gold-plated copper heater well contained a platinum capsule-type resistance thermometer, calibrated by the National Bureau of Standards, within a cylindrical copper heater sleeve carrying 160 ohms of B. and S. No. 40-gauge Advance (constantan) double-fibreglass insulated wire, which was wound bifilarly in double-threaded grooves and cemented in place with " Formvar ". Calorimeter W–6 differs from the usual calorimeter in that a special Monel neck of 15 mm diameter partially isolates the actual lid from the copper calorimeter, and thus allows the lid to be soldered in place with "Cerroseal" solder without appreciably heating the calorimeter or the samples which are placed therein. Calorimeter W–9, used for the adamantane-like compounds, is essentially similar, except that only four vanes are employed. The calorimeter was also tested by measuring the heat capacity of a standard sample of benzoic acid.

## RESULTS OF THE CALORIMETRIC INVESTIGATIONS

*Table 1* provides a summary of the 298·15°K values of the molal heat capacities and thermodynamic functions of the five $C(CH_2X)_4$ compounds studied. Details of the preparation, purification, and characterization of the samples used in these investigations will be reported in a subsequent publication.

Although little of unusual nature was manifest in the other four compounds, a sharp lambda transition of considerable magnitude was found at 249·40°K in $C(CH_2F)_4$, with a heat of transition of 3157·5 $\pm$ 2·3 cal/mole and a molal entropy of transition of 12·7 cal $°K^{-1}$ $mole^{-1}$. The data are also presented graphically in *Figure 1*.

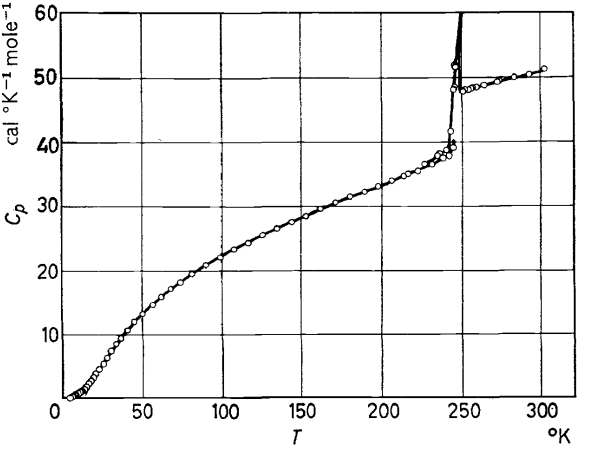



*Figure 1.* The heat capacity of pentaerythrityl fluoride

*Table 1.* Thermodynamic functions at 298·15°K for the crystalline solids (in cal °K$^{-1}$ mole$^{-1}$)

| | $C_p$ | $S°$ | $-\frac{F°-H_0°}{T}$ |
|---|---|---|---|
| $C(CH_2OH)_4$ | 45·51 | 47·34 | 23·16 |
| $C(CH_2F)_4$ | 50·80 | 69·35 | 31·33 |
| $C(CH_2Cl)_4$ | 47·44 | 61·54 | 32·22 |
| $C(CH_2Br)_4$ | 51·10 | 69·58 | 39·45 |
| $C(CH_2I)_4$ | 49·64 | 75·70 | 43·97 |

For adamantane, a sharp lambda-type transition involving 3·9 e.u. was found at 208·6°K. At 298·15°K the heat capacity, entropy, enthalpy increment, and free energy function are 45·46 cal °K$^{-1}$ mole$^{-1}$, 46·80 cal °C$^{-1}$ mole$^{-1}$, 7270 cal/mole, and − 22·42 cal °K$^{-1}$ mole$^{-1}$, respectively.

## DISCUSSION

Perhaps the important group of transitions which result primarily from an orientation of the molecule itself within the crystal structure may loosely be described as " pseudo-rotational " in nature. Only such transitions are presently under consideration. That volume increments, *etc.*, may also result from such transitions is, of course, evident. Before attempting to interpret the data concerning the compounds investigated in this research, and the data available from other sources, it is desirable to consider first what type of relationships should be expected from " pseudo-rotational " transitions in general.

The fusion phenomenon has been discussed by several authors[13, 14] who have shown that the correlations existing between fusion entropy increments are not as clear as would be desired. For elements or simple molecular-type compounds, the entropies of fusion generally lie between 1 to 3 e.u. The entropies of fusion for specific families of elements or classes of compounds existing in the same lattice classification can generally be compared favourably within 0·3 to 0·4 e.u., while the comparisons differ more significantly for such elements or compounds in different lattices.

The disagreement observed in the fusion entropies of similar elements or analogous compounds has generally been attributed to one factor[15]. The lattice structure of any crystal system is dominated by a high degree of long-range order, if the crystal imperfections are not serious. In the process of fusion, the long-range order disappears in favour of a so-called short-range order, which is characteristic of liquids in general. Unfortunately, the short-range order attributed to liquids is apparently not uniform for all liquids, in contrast to the essentially identical degree of long-range order in the crystalline solids. The degree of short-range order is apparently dependent on the size and shape of the atoms or molecules in the liquid state, and on the forces arising from the nature of the element or compound in question. For a homologous series of compounds or a chemically similar series of elements, the discrepancies in the fusion entropies are usually not greater than 0·4 e.u.

Although solid–solid transitions, in contrast to solid–liquid transitions, may involve changes of lattice types, or orientational changes of particular molecular or ionic groups within the crystal, or both, the over-all degree of long-range order of the crystal structure, in general, persists both before and after the transition. Therefore, the type of entropy discrepancies attributed to differing degrees of order in the liquid state should not appear in the factors contributing to the entropy change found in low-temperature transitions. Consequently, in the " pseudo-rotational " transitions, the entropy associated with the change occurring in the symmetry features of the structure, both molecular and crystallographic, should be in agreement with the entropy calculated statistically from the change in the number of symmetry features involved in the transition. Support for this hypothesis is a goal of this research.

**Nitta's interpretation of pentaerythritol**

On the assumption of the above hypothesis, Nitta's treatment of the mechanism of the transition occurring in pentaerythritol[11] originally led to interest in the pentaerythritol transition. It is worthwhile to consider Nitta's approach to the problem before discussing the correlation with experimental results obtained in this laboratory.

First of all, the possibility of complicating positions of the hydroxyl hydrogen atoms in the hydrogen bonds due to a double minimum type of bond is neglected, and the configurational entropy of the low-temperature tetragonal phase of pentaerythritol is assigned the value zero. In the high-temperature cubic phase, however, the configurational entropy due to hydrogen and oxygen is of primary importance and must be taken into consideration. To estimate the entropy due to the hydrogen and oxygen, Nitta assumed, for convenience, a relatively simple model. Assuming three potential minima for a hydroxyl hydrogen atom rotating about a carbon–oxygen bond, as in the case of methanol, and also assuming that each such hydrogen atom is in motion independent of the motions of the rest of the molecule, the contribution due to the hydrogen atom positions is $4\,R\ln 3$. Each of the oxygen atoms is also assumed to have three potential minima about the carbon–carbon bond. However, the positions of the oxygen atoms in the molecule, where the oxygen atoms have very near approach to each other, are considered unlikely, and are omitted from calculation. Thus Nitta considers it possible that, in the cubic phase, there are three relatively stable configurations for the molecule as a unit. Each of these configurations has three orientational possibilities and a value of $R\ln 9$ is assigned for the configurational entropy due to the oxygen atoms in the molecule. Taking further into account that the crystallographic data indicate that the $-CH_20-$ tetrahedra have two configurations, Nitta assigns an additional factor of $R\ln 2$ for this effect. The total configurational entropy of the cubic phase due to hydrogen and oxygen is then, according to Nitta, $R\ln 9 + R\ln 2 + 4\,R\ln 3 = 14{\cdot}47$ e.u.

The entropies of transition and fusion of pentaerythritol are, respectively, 22·8 and 3·2 e.u. These were added and the entropy of fusion of pentaerythrityl bromide, 12·69 e.u., was subtracted, and the resulting value (13·3 e.u.) was compared with the configurational entropy of 14·47 e.u. calculated

above. Nitta states that " the agreement is rather unexpectedly close, for it is evident that the above estimation has been carried out in too simple a fashion . . . ". A disagreement of 1·1 e.u. is, however, greater than would be anticipated on the basis of the hypothesis discussed, if the proper mechanism had been employed.

### Interpretation of pentaerythrityl fluoride

At the time this research work was initiated, only two symmetrically similar comparison substances, neopentane, $C(CH_3)_4$, and the tetramethyl ester of thiocarbonic acid, $C(SCH_3)_4$, had been investigated. Extensive studies carried out on these compounds showed a low-temperature transition in the neopentane, and two transitions below the melting point in the thiocarbonate. Although these two compounds are structurally similar to pentaerythritol, it was felt that a more ideal comparison substance would be found by synthesizing and investigating the properties of pentaerythrityl fluoride. Because of the proximity in size of oxygen and fluorine, it was anticipated that this compound would show a transitional behaviour similar to that of pentaerythritol except for the contributions of the hydroxyl hydrogen atoms. In fact, if the convenient assumptions:

(1) that both pentaerythritol and pentaerythrityl fluoride have the same degree of order in the low-temperature phase, and

(2) that by virtue of nearly equal size, oxygen and fluorine will occupy identical sets of positions in their respective molecules in the high-temperature phases,

are entertained, then the transitional entropy increments of pentaerythritol and of the fluoride would be expected to differ only by the hydroxyl hydrogen contribution. This contribution would be expected to give an increment of $4R$ ln3 from the three positions of minimum energy for each of four hydroxyl hydrogen atoms. However, Nitta's Fourier analysis of the cubic phase of pentaerythritol indicates that the best agreement with the experimental data is obtained if the $-CH_2O-$ tetrahedra are allowed to have two sets of positions, one 180° out of phase with the other. For these two sets of positions for the $-CH_2O-$ tetrahedra there are two independent sets of $3^4$ possible orientations for the hydroxyl hydrogen atoms in pentaerythritol and the entropy contribution should be $R$ ln2 + $4R$ ln3 = 10·15 e.u. If this value is subtracted from the measured transition entropy increment of pentaerythritol (22·8 e.u.), the difference is the calculated value for the transition entropy increment for pentaerythrityl fluoride (12·65 e.u.). The measured value for the pentaerythrityl fluoride transition is 12·66 e.u., in exact agreement with the calculated value.

### Further interpretation of $C(CH_2X)_4$ molecules

This remarkable agreement suggested that it might be possible to account for the symmetry features involved in the entropy increment of 12·66 e.u. for the transition occurring in the fluoride. Since the contribution due to the hydroxyl hydrogen atoms in pentaerythritol has now been eliminated, a general model may be used for consideration of the fluoride, since it is fundamentally a pentaerythritol-like molecule without the hydroxyl hydrogen atoms.

Fischer–Hirschfelder models show that there are seven independent molecular structures for pentaerythritol resulting from all possible orientations of the oxygen atoms, but neglecting the positions of the hydroxyl hydrogen atoms. These seven molecular forms are shown in *Figure 2*. All of the molecular forms except I and II involve oxygen–oxygen approach, which is much too close to allow stability. I and II and the enantiomorph of II, however, are models where all oxygen–oxygen distances are large. Therefore, these are considered to be the only three stable molecular forms.

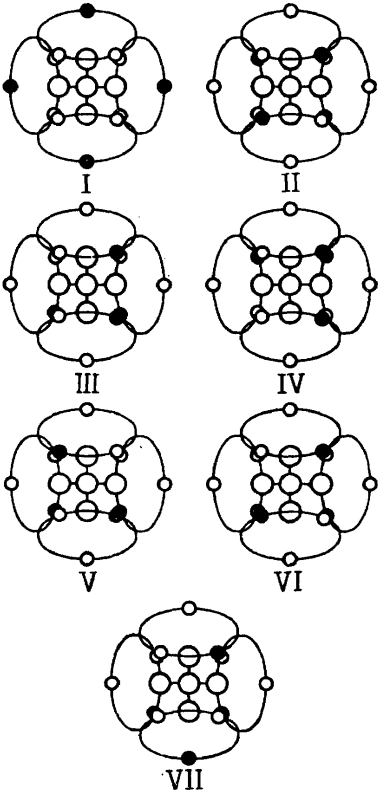



*Figure 2.* Seven molecular structures of pentaerythritol

The indication that two sets of positions are possible for the —$CH_2O$— tetrahedra in pentaerythritol may logically be extended to the —$CH_2F$ tetrahedra in the fluoride. These two sets of positions can be conveniently described as " staggered " or " eclipsed " relative to the skeletal carbon–carbon bonds. No proof can be offered, of course, at the present time that the equilibrium positions do not deviate from these arbitrary choices.

Consider that all the tetrahedra occupy the same set of positions. By reasoning analogous to that employed on pentaerythritol, it is concluded that only three distinct, stable molecular forms exist wherein close approach

of the fluorine atoms to each other is not involved. It is assumed, but not demonstrated, that in single molecules in which some of the $—CH_2F$ tetrahedra occupy different sets of positions, two stable molecular forms will also exist. If each $—CH_2F$ tetrahedron can occupy two sets of positions, then, for four such tetrahedra, the number of configurations of the molecule in the crystal due to these orientations will be $2^4$. For each one of these $2^4$ molecular configurations, there will be, upon neglecting the positions of closest approach for the fluorine atoms, three distinct stable molecular forms, as assumed above, due to the presence of the fluorine atoms in the molecule. Therefore, there are $3 \times 2^4$ stable oriented molecular structures possible in the high-temperature phase. The entropy contributions due to these factors are, therefore, $R$ ln3 for the presence of fluorine in the molecule and 4 $R$ln2 for the orientational possibilities of the $—CH_2F$ tetrahedra.

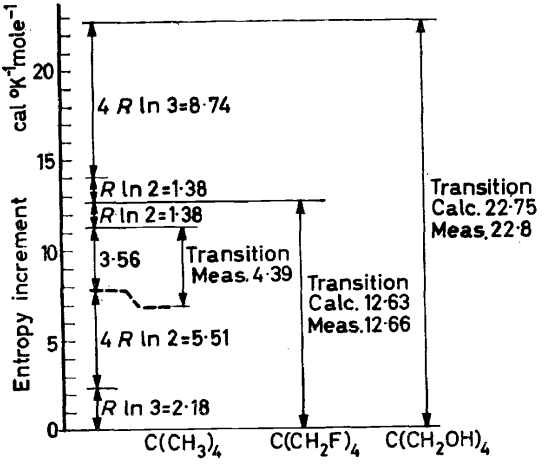



*Figure 3.* Entropy diagram

In addition to these factors, there are two orientational possibilities for the central $—CC_4—$ tetrahedron itself. Since one of the four-fold axes of this tetrahedron lies on a principal crystallographic axis of the cubic phase, the molecule as a whole may be rotated about this axis by 90°, effectively inverting the orientation of the $—CC_4—$ tetrahedron. Consequently, a term of $R$ ln2 must be added for this effect. The total entropy calculated thus far for the transition in the fluoride is $6R$ ln2.

In order to make further comparisons, it is necessary to consider the neopentane transition. The transition at 140°K as measured by Aston and Messerly[7] involves an increment of 4·39 e.u. The heat capacity does not change significantly upon transition, suggesting that there is no change in the molecular structure during the transition. Consequently, the 4·39 e.u. must arise from orientational possibilities, changes in crystal structure, and volume increment effects. If we are permitted to deduct arbitrarily 0·83 e.u. as a difference occasioned by the disparity in molecular size for the two latter effects, then the orientational part of this transformation amounts to 3·56 e.u. It is considered that the similarities between neopentane and

pentaerythrityl fluoride are great enough for the fluoride to exhibit all entropy terms found in neopentane in addition to the terms which may be calculated as due to the nature of the fluoride itself.

The total entropy change for the transition in the fluoride may, therefore, be considered to be the sum of the following entropy terms: 3·56 e.u. for the orientational part of the entropy increment occurring in the transition in neopentane; $R$ ln2 for the orientation of the —$CC_4$— tetrahedron in the fluoride; 4 $R$ln2 for the orientations of the —$CH_2F$ tetrahedra, and $R$ ln2 for the introduction of the four fluorine atoms into the molecule. The total entropy was calculated from these terms to be 12·63 e.u., in excellent agreement with the measured value for the transition entropy of 12·66 e.u. occurring in the fluoride. This general situation is represented graphically in *Figure 3*.

At the present time measurements are being extended to higher temperatures to include the fusion thermal effects and provide an alternative basis for correlation.

## Adamantane

Adamantane was prepared by the method of Schleyer[16]. The crystal structure was investigated by Giacomello and Illuminati[17] and by Nowacki[18]. At room temperature the structure is the face-centred cubic space group $T_d^2$–$F\bar{4}3m$. Further single-crystal X-ray diffractional studies on the forms above and below the transition temperature are at present being conducted in this department by Professor Christer Nordman and should aid significantly in the statistical interpretation of the data.

## Note added in proof

Data and correlation devised subsequently to the oral presentation of this paper on these and related molecules are presented elswhere [19, 20].

## References


[1] L. Pauling. *Phys. Rev.*, **36**, 430 (1930)
[2] J. Turkevich and C. P. Smyth. *J. Am. Chem. Soc.*, **62**, 2468 (1940)
[3] C. P. Smyth. *Chem. Rev.*, **19**, 329 (1936)
[4] G. H. Goldschmidt and D. G. Hurst. *Phys. Rev.*, **86**, 797 (1952)
[5] H. A. Levy and S. W. Peterson. *Phys. Rev.*, **86**, 766 (1952)
[6] C. C. Stephenson *et al.* *J. Chem. Phys.*, **20**, 1046 (1952)
[7] I. Aston and G. H. Messerly. *J. Am. Chem. Soc.*, **58**, 2354 (1936)
[8] I. Nitta *et al.* *Bull. Chem. Soc. Japan*, **13**, 1, 28 (1938)
[9] I. Nitta *et al.* *Proc. Japan Acad.*, **26**, 9, 25 (1950)
[10] I. Nitta *et al.* *Proc. Japan Acad.*, **26**, 10, 11 (1950)
[11] I. Nitta *et al.* *Proc. Japan Acad.*, **26**, 10, 19 (1950)
[12] E. F. Westrum *et al.* *J. Chem. Phys.*, **21**, 419 (1953)
[13] O. Kubaschewski. *Trans. Faraday Soc.*, **45**, 931 (1949)
[14] A. R. Ubbelohde. *Quart. Rev. (London)*, **4**, 356 (1950)
[15] R. A. Oriani. *J. Chem. Phys.*, **19**, 93 (1951)
[16] P. V. R. Schleyer. *J. Am. Chem. Soc.*, **79**, 329 (1957)
[17] G. Giacomello and G. Illuminati. *Ricerca sci.*, **15**, 559 (1945)
[18] W. Nowacki. *Helv. Chim. Acta*, **28**, 1233 (1945)
[19] E. F. Westrum Jr. *J. Phys. Chem. Solids*, **18**, (1), 83 (1961)
[20] S. S. Chang and E. F. Westrum, Jr. *J. Phys. Chem.*, **64**, 1547 (1960); **64**, 1551 (1960)